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14. ABSTRACT This DURIP proposal was funded to upgrade an existing Kratos Ultra Axis X-ray Photoelectron Spectrometer (XPS) in the Penn State Materials Characterization Laboratory Facility as the primary objective along with an existing RHK, ultrahigh vacuum atomic force microscope (AFM) in the Allara lab as the secondary objective. These acquisitions allow new capabilities for performing experiments directed at synthesizing novel types of discrete heteroatom clusters by highly controlled vapor deposition and understanding critical interfacial chemistry					
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a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER 814-865-2254

Report Title

Upgrading of Existing X-Ray Photoelectron Spectrometer Capabilities for Development and Analysis of Novel Energetic NanoCluster Materials (DURIP)

ABSTRACT

This DURIP proposal was funded to upgrade an existing Kratos Ultra Axis X-ray Photoelectron Spectrometer (XPS) in the Penn State Materials Characterization Laboratory Facility as the primary objective along with an existing RHK, ultrahigh vacuum atomic force microscope (AFM) in the Allara lab as the secondary objective. These acquisitions allow new capabilities for performing experiments directed at synthesizing novel types of discrete heteroatom clusters by highly controlled vapor deposition and understanding critical interfacial chemistry in compositions of nanoscale materials in highly energetic nanostructures.

Project funding period ended 05/31/07. Equipment was all purchased by the end of the funding period and the installation and trials completed by 09/27/08. Research using the upgraded instruments and capabilities has started. Pictures and results illustrating the equipment upgrade on the XPS system are shown below. The first experiments in the AFM system are now being done with systems of Al atoms on nitro-containing molecules and polymer films.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
David Allara	0.00
FTE Equivalent:	0.00
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PhDs

<u>NAME</u>

Total Number:

Names of other research staff

<u>NAME</u>

<u>PERCENT SUPPORTED</u>

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Final Report

Grant #: W911-NF-1-0224

Grant Period: June 01, 2007 To May 31, 2008

Title: Upgrading of Existing X-Ray Photoelectron Spectrometer Capabilities for Development and Analysis of Novel Energetic NanoCluster Materials (DURIP)

PI Name: David L. Allara

Department: Chemistry and Materials Science & Engineering

Institution: Pennsylvania State University, University Park, PA 16802

Introduction

The original proposal was written to request funding to upgrade an existing Kratos Ultra Axis X-ray Photoelectron Spectrometer (XPS) in the Penn State Materials Characterization Laboratory Facility as the primary objective to upgrade an existing RHK, ultrahigh vacuum atomic force microscope (AFM) in the Allara lab as the secondary objective. The purpose of these acquisitions was to allow new capabilities for performing experiments directed at synthesizing novel types of discrete heteroatom clusters by highly controlled vapor deposition and understanding critical interfacial chemistry in compositions of nanoscale materials in highly energetic nanostructures. This work was primarily directed towards support of ongoing work in the existing ARO funded MURI on Nanoenergetic Materials, *A Unified Multiscale Approach for Nano-Engineered Energetic Materials* (NEEM; Grant #W911NF-04-1-0178) with some additional collaborative work with the ARO funded MURI, *Superatoms of Building Blocks of New Materials*, under the direction of Professor W.A. Castleman. In both these projects a central theme was to produce stabilized nanoscale building blocks of highly energetic materials, e.g., Al fuels, that eventually could be compounded in various hierarchical structures with oxidizers to provide new classes of highly controllable energetic properties. One promising direction towards this objective was to prepare stable clusters on well defined surfaces and thin films by atom flux deposition. Two key diagnostics for the processing of these novel layer structures are x-ray photoemission (XPS), primarily giving electronic and chemical characteristics along with atom coverage, and atomic force microscopy (AFM), primarily giving local morphology characteristics. Involved in these ideas were the concepts of using combinations of reactive atoms such as Al + K that could result in partial stabilization for handling and eventual assembly and also could yield new energetic characteristics for different oxidizers, as well as intermetallic energetic materials.

The key equipment items of interest at the time of proposal submission are listed in Table 1.

Table 1

#	Item
1	CE-5218 Delay Line detection system for an existing Kratos AXIS Ultra XPS instrument (located in the Penn State Materials Characterization Laboratory, next to the PI's lab)
2	Atom Vapor effusion cells:
2A	10-HT effusion cell with flange connections 2 crucibles; including power supply, & pneumatic shutter
2B	Pfeiffer TMU 261P 210 L/s Turbomolecular Drag Pump for use with the atom sources
3	SPM 1000 Rev 8.5 upgrade for an existing high resolution, uhv AFM system in the PI's lab
4	2 SG0150PC gate valves for atom source interfacing
5	2 Thin film deposition systems including: monitor, sensor, feedthru, accessory kit for atom deposition monitoring
6	Cryo-Plex 8 cryopump and compressor for the XPS atom deposition forechamber

Results and Accomplishments for Equipment Purchase and Installation

The equipment purchasing was spread out over a number of months partially because of vendor requirements and partly in order to constantly update the priorities and changing requirements as the items were assembled into the major instrumental and tool setups for the actual research applications (funded under other grants). Because of price changes by Kratos it was possible to fully upgrade the XPS with both the new detector system (item 1) and a temperature dependent probe that could be used for T-dependent studies of metal atom/organic interactions. An illustration of the new setup along with a trial experiment on thermal decomposition of an thin oxidizer film is shown in Figure 1A,B.

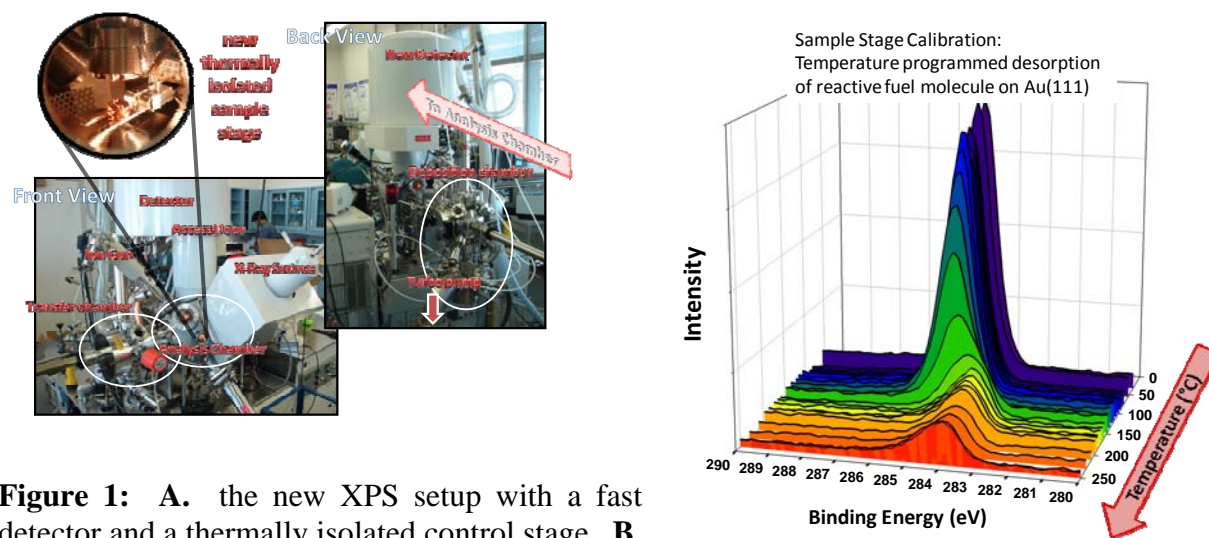
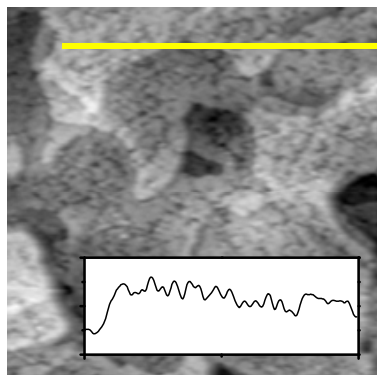


Figure 1: **A.** the new XPS setup with a fast detector and a thermally isolated control stage. **B.** A demonstration of following the XPS spectra (C 1s line) as a function of temperature for an organic monolayer.

The XPS system also has a side chamber added for the metal atom depositions interfaced with a uhv loadlock sample transfer system for moving the sample under continuous vacuum into the analysis chamber (see circled area in front of **B**). The side chamber utilizes a turbopump and cryopump (items 2B & 6), a gate valve (item 4) and a thickness monitor (item 5). Due to the eventual need for

added flexibility in depositing a larger range of atoms than originally thought (for example, adding B to the list), a decision was made to not order the more restricted capability (though higher performance) Knudsen effusion cells and rather to utilize existing portable e-beam sources. The remaining funds were then used for vacuum parts and electronics to utilize the e-beam sources in tandem with other types of thermal sources (e.g., deposition boats for alkali metals such as K).

The high resolution AFM was also upgraded with new electronics to allow high resolution non-contact (NC) scans on delicate samples with metal atom nanoclusters on the surface that would otherwise be easily pushed across the surface with standard contact scanning. An example of a NC image of the surface of a thin film of Al metal nanoclusters deposited on a well-ordered hydrocarbon



type self-assembled monolayer surface is shown in Figure 2. The figure (0.4 μm x 0.4 μm scan range) shows the general features of Au(111) terraces underlying the conformal monolayer.

In addition, the use of NC mode allows the imaging of very small ~ 1 -2 nm Al metal clusters scattered across the surface. If typical contact mode were used the surface would be swept free of the clusters and the surface would appear smooth to within ± 0.1 nm or so. A publication has been submitted based on this work. The actual work was funded under the main MURI NEEM grant so is not reported here.

Figure 2. A non-contact mode AFM scan of the surface of an ordered hydrocarbon self-assembled monolayer with scattered clusters of deposited Al atoms across the surface. Without the use of NC to avoid sweeping the clusters they could not be observed.

Relevance to Army Needs and Mission

Research enabled by this equipment purchase (research funded separately) is now being directed towards benefits in understanding mechanisms of and developing improved control for nanoenergetic materials used as propellants and explosives.

Collaborations and Technology Transfer

- N/A
- N/A

Resulting Journal Publications During Reporting Period

- N/A for this grant

Graduate Students Involved During Reporting Period

- N/A

Awards, Honors and Appointments

- N/A